Respirometric In Situ Methods for Real-Time Monitoring of Corrosion Rates: Part II. Immersion

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With the aim to open a new window into corrosion processes this paper presents respirometric methods for real-time in situ monitoring of corrosion rates under immersion conditions. With these techniques, sensitive, non-destructive corrosion rate measurements are possible on basically all metals and alloys. Different methods are presented that enable to monitor HER, ORR or both reactions simultaneously based on the amount of evolved H_2 or the amount of consumed O_2 by volumetric, manometric and sensor-based approaches. Various research examples are presented, demonstrating the benefits and limitations of the different approaches. For Mg alloys, besides HER, ORR plays a role in the cathodic reactions and a good correlation of the total cathodic charge with mass loss was obtained. H_2 dissolution into the electrolyte was identified as an important factor. The results obtained for Zn immersion corrosion in intermittent-flow and flow-through respirometric experiments suggest that the ORR mechanism leads to the generation of stable H_2O_2 under these conditions. As a result, the effective number of exchanged electrons for one O_2 molecule was found to be in between two and four. The here introduced respirometric techniques allow new insights into corrosion mechanisms, in addition to enabling real-time monitoring of corrosion.

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Manuscript submitted November 20, 2020; revised manuscript received January 12, 2021. Published January 22, 2021. *This paper is part of the JES Focus Issue on Characterization of Corrosion Processes in Honor of Philippe Marcus.*

Supplementary material for this article is available [online](#)

This paper is the second of a series that describes the use of respirometric approaches in corrosion science. While Part I covered techniques to monitor atmospheric corrosion in real-time,¹ this part is focused on immersion conditions. In Part III respirometric methods will be combined with electrochemical measurements and the methods will be applied to follow changes of the immersion conditions in real-time, directly on the same sample.

Full immersion conditions are frequently used to study corrosion of metallic materials. One advantage of immersion tests is that the bulk electrolyte facilitates the use of electrochemical techniques to characterize a corrosion process. The methods employed range from macroscopic electrochemical techniques like potentiodynamic polarization (PP), linear polarization resistance measurements (LPR), electrochemical impedance spectroscopy (EIS) and electrochemical noise measurements (EN) to localized electrochemical techniques like scanning vibrating electrode (SVET), scanning droplet cell (SDC), and others. Each technique shows different possibilities and limitations and a complementary approach is useful to reveal many details about the studied corrosion system.²

Additionally, non-electrochemical techniques are commonly used to quantify the amount of corrosion that occurs during immersion. This includes the gravimetric determination of mass loss after removal of the corrosion products with a suitable pickling solution.³ The quartz crystal microbalance (QCM) can be used to monitor mass changes with a high resolution in situ.^{4,5} Another approach is the detection of metallic cations released into the immersion electrolyte by solution analysis, e.g. with ion chromatography (IC),⁶ inductively coupled plasma atomic emission spectroscopy (ICP-AES), or mass spectrometry (ICP-MS). Sophisticated in-line techniques for both ICP-AES^{7,8} and ICP-MS^{9,10} have been developed that allow for monitoring of time- and potential-resolved elemental dissolution rates. While insoluble species that form a corrosion product film are undetectable by ICP-AES, there are cases where the amount of insoluble ions may be quantified indirectly by a mass-charge balance during galvanostatic experiments.⁸

While some of the methods mentioned above are destructive and only give information at a distinct point in time (PP) or the cumulative

or historical amount of corrosion that has occurred (mass loss, off-line solution analysis), other methods are capable of monitoring the corrosion process in the time domain (LPR, EIS, EN, QCM, in-line spectrometry). However, to extract reliable corrosion rates with these methods is not without pitfalls. For example, in PP, significant variability of the results comes from the selection of the linear regions where to perform the Tafel fit. Influence of mixed activation control and diffusion control can be an issue,¹¹ as well as contributions of ohmic drop¹² that are difficult to assess accurately. Additionally, it is required to polarize the sample far away from its free corrosion potential in order to determine the correct Tafel slopes. This strong polarization can lead to changes induced on the sample surface that can affect the results. The alkalization related with cathodic reactions can artificially increase or decrease the dissolution rate. Therefore, it can make a difference whether the scan is started at a cathodic potential or at the corrosion potential.¹³ For Mg, it was found that Tafel extrapolation from the cathodic polarization initiated at the corrosion potential provides a good estimate of the corrosion rate while starting the potential scan at a cathodic potential leads to substantial underestimation of the corrosion current.¹⁴ For Al, cathodic dissolution can occur during the cathodic scan as a consequence of the produced OH^- that attacks the native oxide film.^{13,15–17}

The interpretation of data generated with EIS or LPR can be challenging as well. A suitable electrical equivalent circuit that represents the correct physicochemical processes of the corroding electrochemical interface is needed for the extraction of a polarization resistance value. The polarization resistance, obtained from fitting EIS data to an equivalent circuit or from LPR measurements, can be inserted into the Stern-Geary equation to obtain instantaneous corrosion rate information. For this however, the Tafel slopes are another required input that has to be determined with independent experiments.¹⁸ Changes of these values with time are usually not considered which makes interpretation of data from the Stern-Geary method difficult.¹⁹ Another issue complicating EIS measurements is the intrinsic non-stationarity of a corrosion process that is most severe in the time directly after immersing the sample.²

Respirometry is a widespread method used in many research disciplines to quantify metabolic rates associated with the respiration of animals,^{20,21} plants,^{22,23} tissues,²⁴ cells,²⁵ or microorganisms.²⁶ Metabolic processes in a biochemical sense are redox reactions that involve the transfer of electrons from donor molecules (e.g. organic

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compound) to an electron acceptor (e.g. O_2) in order to provide the organism with energy.²⁶ The respirometric principle is based on measuring the rate of the reduction reaction associated with this metabolic conversion process.²⁶ For example, the consumption of O_2 by a fish in a sealed chamber can be measured to characterize its metabolism under different conditions.²⁷ In a way, corrosion is a similar redox process that is composed of an anodic metal oxidation reaction and a cathodic reduction reaction that occur at an equal rate on the corroding surface. The aim of this paper is to demonstrate that similar respirometric approaches can be employed to monitor corrosion rates under immersion conditions non-destructively and in real-time by monitoring the rate of the cathodic reactions. Different methods to assess the rate of the O_2 reduction reaction (ORR)^{28–30} or the H_2 evolution reaction (HER)^{14,31,32} of immersed samples have been presented before. However, the use of this universal approach, that is applicable in principle to all metals or alloys,³⁰ in quantitative corrosion studies remained below its potential. This paper gives an overview of the different approaches and additionally presents new methods that enable one to monitor ORR, HER or both reactions simultaneously. Furthermore, it is intended to highlight details in the experimental setups that are necessary to avoid typical pitfalls and to get reliable results. The possibility to apply the method to study biodegradable metals in different simulated physiological solutions is shown. Examples of measurements with different respirometric methods will be presented and are compared with independent mass loss measurements.

Respirometric Approach

As described in Part I of this paper series, the measurement principle of the respirometric method is to monitor the rates of the most important cathodic reactions (HER and ORR) based on the measurement of the rates of O_2 consumption or H_2 evolution. In the HER protons are reduced to H_2 gas (Eq. 1).

The mechanism of the ORR, which involves several elementary steps and reaction intermediates, has been controversially discussed and is still not completely resolved.³³ According to a simplified reaction scheme,³⁴ the reduction of O_2 can progress by two alternative pathways depending on the electrocatalytic material where the reaction takes place.^{35–37} O_2 can be reduced in a direct 4-electron mechanism (Eq. 2) to H_2O without any detectable intermediates. The parallel peroxide pathway includes the reduction of O_2 to H_2O_2 as an intermediate (Eq. 3), that can be followed by a further reduction of the peroxide (Eq. 4) or by decomposition of two H_2O_2 molecules via a disproportionation reaction (Eq. 5) to O_2 and H_2O . Alternatively, H_2O_2 can be transported to the bulk solution. Hence, for the ORR, the effective number of exchanged electrons z_{ORR} can range between $z_{ORR} = 2$ (incomplete reduction with only reaction 3) and $z_{ORR} = 4$ (direct reduction or complete reduction with a combination of reactions 3 + 4 or 3 + 5).³⁷ As a consequence, the number of metal ions that can be oxidized by one O_2 molecule can vary by a factor of two which contributes uncertainty to ORR rates calculated from O_2 consumption rates.

The respirometric measurement approaches discussed in this work for immersion can be categorized in volumetric techniques, manometric techniques or the measurement of partial pressure or concentration with a sensor (Fig. 1). In the volumetric approach, changes in gas volume are detected at ambient pressure, while in the manometric approach changes in pressure are measured in constant volume chambers. As opposed to atmospheric corrosion, a bulk liquid phase is present in immersion conditions. The species dissolved in this phase have to be taken into account, when determining the rate of consumption of O_2 or the rate of production of H_2 that accompanies a corrosion process. Some techniques that

Figure 1. Classification of respirometric approaches to monitor immersion corrosion kinetics by the measurement principle and the degree of flow. Arrows in the lower part of the figure visualize the degree of flow through the respirometric chamber for the different measurement approaches. Adapted from Ref. 1.

will be presented require the presence of a gas headspace above the liquid phase. The partial pressure of O₂ and H₂ gas in this phase have to be determined and included in the mass balance.

To prevent depletion of O₂ which can occur in prolonged experiments, the concepts of flow-through respirometry²⁰ or intermittent-flow respirometry³⁸ can be adapted. Compared with static immersion conditions, a flow cell setup brings new possibilities to study corrosion processes. On the one hand, a flowing electrolyte enables keeping the exposure conditions constant that would be subject to change in a closed system. There, ongoing corrosion can lead to changes in the electrolyte composition like the depletion of dissolved ions or O₂, changes in the bulk pH of the electrolyte, or accumulation of dissolved metal ions. On the other hand, a respirometric flow cell can be used to change the exposure conditions while providing real-time data of the effects on the corrosion rate. Particularly, the electrolyte composition can be changed with respect to e.g. chloride concentration. Another application is to study the effect of the addition of different concentrations of inhibitors, or to elucidate the role of amino acids or other organic molecules present in electrolytes that are commonly used to test biodegradable metals *in vitro*. In this context it is also possible to realize a change of the temperature of the experiment to values that will be present in the human body. In addition, also the effect of the flow rate on the corrosion rate can be of interest for biodegradable cardiovascular stents or other applications.

Microbial background respiration, i.e. the consumption of dissolved O₂ that is not related to the studied corrosion process has to be avoided or determined by experiments without a sample. This aspect can be critical if solutions are studied that contain nutrients for microorganisms. Apart from cleaning and disinfection of the setup, sterilization of the solution or frequent exchange of the solution can help to control interference of background respiration. Other important factors are the construction material of the respirometer and its surface area to volume ratio.³⁹ The biofilm formation is also dependent on the temperature⁴⁰ and pH⁴¹ of the solution.

Electrolytes that contain oxidants other than O₂ or water, e.g. nitrate, cannot be studied with the presented setups and would require additional sensors to be analyzed with the respirometric method. Pre-corroded Fe samples were shown to reduce Fe³⁺ ions in the rust scale as a cathodic process parallel to ORR under atmospheric corrosion conditions.⁴² This implies that data generated with respirometric O₂ consumption measurements on pre-corroded Fe initially after immersion should be treated with caution. As the amount of reducible Fe³⁺ in the corrosion products is limited, a steady state ORR rate should be established at some point. Additionally, the evolution or consumption of other gases not related to corrosion has to be excluded. For example, this could be the case for electrolytes supersaturated with HCO₃⁻ that can liberate CO₂ gas.

Volumetric techniques.—Monitoring HER rates volumetrically is well established to study, e.g. Mg or Al corrosion.^{14,15,32} The volume of H₂ gas evolved from the sample can be measured for example with a setup containing a funnel inserted in an inverted burette, initially filled with electrolyte (Fig. 2a). Gradually, the electrolyte gets displaced by the collected H₂ gas and the volume can be obtained from the burette reading. A more sensitive gravimetric technique (Fig. 2b) was first presented by Curioni¹⁴ and further developed by Fajardo and Frankel.⁴³ In this setup, a collection container is submerged together with the sample and both are connected to a balance. A change of the gas volume under the collection container causes a change in buoyancy that can be measured as a weight change with the balance. The benefit of the gravimetric method over the burette setup is that it provides a higher sensitivity, better time resolution and improved collection efficiency, as also H₂ bubbles that stick to the sample are registered.⁴³

One possible source of error with these open systems is a loss of H₂ gas by dissolution into the electrolyte and to the ambient air that

can lead to an underestimation of the amount of detected H₂. Pre-saturation of the electrolyte could resolve this issue for short-term experiments but is another step that complicates the experiment. Moreover, pre-saturation by bubbling with pure H₂ gas leads to the unintended displacement of dissolved O₂, while pre-saturation by electrolyzing chloride containing solutions can lead to pH changes and the generation of reactive chlorine species at the anode which could influence the corrosion mechanism.⁴⁴ Figure 2c shows the schematic of a gravimetric setup with reduced volume of electrolyte that was designed in this study to minimize the dissolution of H₂ into the electrolyte. An air headspace separates the electrolyte in contact with the sample from the electrolyte that is necessary for complete submersion of the collection assembly. That way, the dissolution of H₂ is limited to a high extent to the small volume of the immersion electrolyte. As an alternative to the air headspace, the immersion volume can be confined with a flexible rubber barrier (Fig. 2d) that must be able to adapt to volume changes without the build-up of a pressure.

The gravimetric setup can be used also to monitor samples that show only O₂ consumption and negligible HER rate. As the dissolved O₂ cannot be detected with the buoyancy method, an air headspace is required and the consumption of O₂ gas from that headspace is monitored by the volume reduction gravimetrically. Because of the gas exchange at the liquid–gas interface, the consumption of dissolved O₂ by the corroding sample leads to a depletion of O₂ also in the gas phase that can be readily detected with the balance. The addition of a flexible rubber barrier is necessary for limiting the exchange of dissolved O₂ with the surrounding solution (Fig. 2d). Monitoring both HER and ORR simultaneously with the volumetric setup is feasible with the addition of an optical O₂ sensor that determines the partial pressure of O₂ in the headspace non-invasively through the vessel wall without touching the collection container.

The volume of the collection assembly and the volume of air initially present at the beginning of the experiment can be determined from buoyancy considerations as described in a previous paper.⁴⁵ To correct for changes in the gas volume that are solely caused by changes in temperature and atmospheric pressure, these quantities have to be logged throughout the experiment. The correction is described in more detail in earlier work.⁴⁵ Another influence on the measurement is the density of the solution that depends on the amount of dissolved salts and temperature. According to Archimedes' principle, the change in the volume of the gas $V_{gas}(t)$ is directly related to the measured change in the apparent weight of the collection container $W_{balance}(t)$ by:

$$V_{gas}(t) = -\frac{W_{balance}(t)}{g \rho_{solution}(t)} \quad [6]$$

where $\rho_{solution}(t)$ is the density of the solution and g is gravitational acceleration. The gas volume increases for HER and decreases for ORR and hence, the apparent weight will decrease or increase, respectively. The pressure of the gas is given mainly by the actual atmospheric pressure $p_{atm}(t)$. The hydrostatic pressure of the water column may be neglected for small immersion depths and dilute solutions.⁴³ Water vapor occupies part of the volume, so its partial pressure $p_{H_2O}(t)$ has to be subtracted from the atmospheric pressure. With ideal gas law, and taking into account the above influences, the change in the amount of substance of gas under the collection container can be calculated.⁴⁵

$$\Delta n = \frac{(p_{atm}(t) - p_{H_2O}(t))\Delta V_{gas}(t)}{RT(t)} \quad [7]$$

$\Delta n(t)$ will increase in the case of HER and decrease for ORR as a cathodic reaction. For mixed HER and ORR the O₂ partial pressure changes $\Delta p_{O_2}(t)$ can be determined from parallel optical O₂ measurements in order to determine the amount of consumed O₂.

Figure 2. Schematic representation of immersion respirometric setups: (a) inverted burette volumetric setup, (b) experimental setup for gravimetric H₂ collection, (c) volume reduced gravimetric setup for volumetric respirometric measurements and (d) flexible rubber barrier respirometric setup to separate the immersion electrolyte from the surrounding solution. With an optical O₂ sensor simultaneous monitoring of HER and ORR is possible with setup (d).

Changes in the amount of substance are converted to cathodic charge with Faraday's law (Eq. 8), where z is the number of exchanged electrons and F is the Faraday constant. Taking the derivative of the charge vs time curve results in the HER or ORR current.

$$\Delta Q_{HER/ORR}(t) = \Delta n_{H_2/O_2}(t) \Delta z_{HER/ORR} \cdot F \quad [8]$$

Manometric technique.—A manometric respirometric approach to monitor HER and ORR rates simultaneously in immersion conditions is shown in Fig. 3a. The sample is immersed in a closed chamber with a fixed volume with a gas phase above the liquid phase. A combined sensor for pressure, temperature and relative humidity (RH) is placed in the gas headspace above the solution to measure HER rates. The amount of O₂ in the gas phase can be monitored with an optical O₂ sensor. The amount of O₂ in the liquid phase can be either measured with a second optical O₂ sensor or it can be assumed that both phases are in equilibrium. Then, the

concentration of O₂ dissolved in the liquid phase can be calculated from the partial pressure in the gas phase. The solubility of O₂ in the electrolyte is a function of O₂ partial pressure, salinity and temperature and can be estimated with empirical equations.⁴⁶ The validity of the equilibrium assumption should be carefully checked by determining the concentration with a second O₂ sensor.²⁶ The rate of gas exchange between the gas and liquid phase is determined by the area dimension of the interface which is given by the geometric dimension of the chamber. One of the most important factors affecting the exchange velocity of a sparingly soluble gas such as O₂ is the degree of mixing of the liquid phase.^{47–49} Apart from acceleration of gas exchange, mixing is also important to ensure that the measured concentration of O₂ corresponds to the mean concentration value of the liquid phase.^{38,39} Gradients in O₂ concentration would otherwise lead to incorrect calculations of O₂ consumption rates.

To determine the amount of consumed O₂ molecules $\Delta n_{O_2}(t)$, besides partial pressure changes in the gas phase $\Delta p_{O_2}^{gas}(t)$, changes in the concentration of O₂ dissolved in the liquid phase $\Delta C_{O_2}^{liq}$ have

Figure 3. Schematic representation of immersion experimental setups: (a) simultaneous monitoring of HER and ORR rates with a static, manometric respirometric method and (b) monitoring of ORR rates with an intermittent-flow respirometric method.

to be considered.

$$\Delta n_{O_2}(t) = \Delta n_{O_2}^{gas}(t) + \Delta n_{O_2}^{liq}(t) = \frac{\Delta p_{O_2}^{gas}(t) \cdot V_{gas}}{R \cdot T(t)} + \Delta C_{O_2}^{liq} \cdot V_{liq} \quad [9]$$

with V_{gas} and V_{liq} being the volume of the gas phase and liquid phase, respectively, and R is the ideal gas constant.

The rate of H₂ evolution is determined by the pressure increase inside the closed chamber. As shown in the previous part of the paper, the HER charge can be calculated from the change in the total pressure inside the chamber $\Delta p_{tot}(t)$ with a combination of ideal gas law (Eq. 10) and Faraday's law (Eq. 8). Therefore, the changes in O₂ partial pressure $\Delta p_{O_2}^{gas}(t)$, water vapor pressure $\Delta p_{H_2O}(t)$ and temperature of the gas phase $T(t)$ have to be also taken into account. The temperature of the experiment should be maintained constant or measured at the position of the gas volume. Accurate temperature recording is a prerequisite for both the calculation of the amount of gas molecules, as well as for the internal automatic temperature compensation of the optical O₂ sensor.

$$\Delta n_{H_2}(t) = \frac{(\Delta p_{tot}(t) - \Delta p_{O_2}^{gas}(t) - \Delta p_{H_2O}(t)) \cdot V_{gas}}{R \cdot T(t)} \quad [10]$$

Water is virtually incompressible compared to a gas. Thus, a smaller gas phase volume inside the chamber leads to faster pressure changes and to an improved detection limit.

The evolution of RH inside the gas volume can be measured in situ by the RH sensor with the manometric setup. This allows calculation of the water vapor pressure $\Delta p_{H_2O}(t)$ from the saturation vapor pressure $p_{H_2O}^{sat}$ which is a function of temperature (Eq. 11).

$$p_{H_2O}(t) = RH(t)p_{H_2O}^{sat} \quad [11]$$

The amount of dissolved H₂ can be estimated with Henry's law:

$$C_{H_2}^{diss} = H \cdot p_{H_2}^{gas} \quad [12]$$

Here, H is Henry's law solubility constant, $C_{H_2}^{diss}$ is the concentration of H₂ in the aqueous phase, and $p_{H_2}^{gas}$ is the partial pressure of H₂ in the gas phase under equilibrium conditions.

A conservative estimation for this calculation is to use the actual H₂ partial pressure in the gas phase that was provided by the pressure increase. Regarding the H₂ distribution between gas and liquid phases, significant supersaturation with respect to Henry's law was observed which was attributed to a major resistance to H₂ transfer from the liquid phase to the gas phase.⁵⁰ An upper boundary for the amount of dissolved H₂ is given assuming a partial pressure of H₂ that is equal to the total pressure inside the chamber. This can be rationalized by the fact that the H₂ bubbles evolved from the sample surface are initially pure H₂ before they rise up to the gas headspace. This means that the solution around these bubbles equilibrates with H₂ under a partial pressure close to the total pressure. The true amount of dissolved H₂ will be in between these

two scenarios and probably closer to the lower limit. Taking into account the concentration of O_2 and H_2 in both phases allows for a full mass balance. The actual rates of both HER and ORR can be obtained from the slope of the respective charge curves. Thus, the total respirometric corrosion rate is the sum of both HER and ORR rates.

Intermittent-flow ORR Monitoring.—Corrosion systems that corrode mainly with ORR and not with visible H_2 gas evolution can be monitored by an O_2 sensor approach as shown in Fig. 3b. The consumption of O_2 by a sample that is immersed in a completely filled chamber with a fixed volume of electrolyte is determined, e.g. with an optical O_2 sensor. For very low corrosion rates it might be sufficient to use static exposure in a completely closed chamber. However, for higher corrosion rates or prolonged exposure, the level of O_2 in the solution needs to be restored periodically. In intermittent-flow respirometry this is achieved by periodically flushing the chamber with fresh, air saturated solution. The O_2 consumption rate can be determined from the slopes of the O_2 concentration decrease during each measurement phase of the sawtooth curve together with the volume of electrolyte in the chamber. The fundamental principles that need to be considered when designing and carrying out automated intermittent-flow respirometry measurements are accurately described by Svendsen et al.³⁸ For this kind of experiment the chamber does not need to be hermetically closed. Rather, the chamber has two ports for an inlet and outlet of electrolyte flow. One-way flow valves can be used to avoid the exchange of O_2 with the surrounding reservoir bath. The same function can be provided by inlet tubing of sufficient length and by designing the outlet as an overflow that is positioned above the liquid level of the electrolyte reservoir bath.²⁷ The flush pump can be triggered automatically with a given time interval or when a defined critical O_2 concentration is reached in the chamber. Again, mixing of the solution is important in order to avoid concentration gradients. Mixing can be achieved by stirring the solution or by using a pump inside the chamber, or in a separate recirculation loop.³⁸ In the case of a separate recirculation loop, the total liquid volume comprises the chamber volume plus the volume in the recirculation loop. What should be kept in mind is that the degree of agitation also influences the corrosion rate. Stirring the solution increases the rate of diffusional mass transport of O_2 by decreasing the thickness of the Nernst diffusion layer.

Gas bubbles inside the chamber should be avoided as they provide a possible source or sink for O_2 . Therefore, the outlet should be positioned on the topmost part of the chamber and designed in a way to facilitate the removal of gas during flush phases. If the fountain of water from the overflow is not sufficient to hold the O_2 concentration level of the reservoir close to saturation, the reservoir bath can be aerated with an air pump. Possible background O_2 consumption by microbial activity can be measured in a parallel chamber without sample that is periodically flushed with the same solution as the sample chamber.

Continuous flow-through techniques.—Another approach is to use a continuous flow of electrolyte that passes the corroding sample in a respirometric chamber (Fig. 4). The concentration of dissolved O_2 in the electrolyte is measured in the incurrent ($C_{O_2}^{in}$) and excurrent ($C_{O_2}^{ex}$) stream. The rate of O_2 consumption can be calculated from the concentration difference together with the flow rate $\dot{V}$ and converted to a current with Faraday's law:

$$I_{ORR} = (C_{O_2}^{in} - C_{O_2}^{ex}) \cdot \dot{V} \cdot z_{ORR} \cdot F \quad [13]$$

The flow rate is an important parameter that should be accurately controlled or measured. Sensor drift can be an issue that impairs oxygen readings, especially if two sensors are used. This sensor-based error can be reduced by utilizing a valve system that allows the same probe to sample both streams.³⁸

Figure 4. Flow-through respirometric setup to monitor ORR rates based on the measurement of O_2 concentration in a stream of electrolyte before and after passing a corroding sample in a chamber.

Another issue to be considered for flow-through measurements is that changes in the corrosion rate on a short time-scale are not instantly reflected in the response due to a lag in time and mixing problems.^{21,38} These washout characteristics depend on the ratio of flow rate to chamber volume of the respirometry system and can usually be satisfactorily corrected mathematically.^{21,51} Ignoring the washout characteristics of the system may result in misinterpretation of the obtained results.²⁰ Decreasing the flow rate would increase the signal of the excurrent O_2 sensor which increases the sensitivity of the measurement. However, it takes more time until the measurement responds to changes in O_2 consumption rate due to washout.²⁰

Systems that corrode mainly with HER as a cathodic reaction can be monitored in a flow-through cell with a gravimetric H_2 collection experimental setup similar to the one presented by Han et al.⁵² The H_2 gas bubbles evolved from the corroding sample in a respirometric chamber are transported with the flow of electrolyte. The flow outlet is directed under a submerged collection container that detects the amount of H_2 gravimetrically with a balance. The collected H_2 gas exerts a buoyant force that can be monitored as a change in the apparent weight of the collection container. Care must be taken that bubbles are not retained in bends or junctions. Because the H_2 exits the tubing discontinuously as discrete bubbles, the weight curve shows a step-like course. What must be kept in mind is that H_2 gas is soluble in water. Therefore, depending on the flow rate, much of the generated H_2 is dissolved and hence not detected with the gravimetric measurement.

Combining both flow-through approaches to monitor HER and ORR simultaneously is not advisable because the evolved H_2 gas takes up O_2 from the solution. Even if no O_2 is consumed by corrosion the second O_2 sensor will detect a lower amount of dissolved O_2 in the excurrent stream, thus, suggesting ORR activity that is not real.

Experimental

Materials, sample preparation and electrolytes.—Die cast high purity Mg alloy AM50 and AZ91 plates with a thickness of 2 mm were supplied by DGS Druckgussysteme AG, Germany. High purity AZ31 sheet material was obtained from MgF Magnesium Flachprodukte GmbH, Germany. Zn foil (0.125 mm thickness, purity 99.99%, typical analysis ppm: Fe 19, Cd 19, Pb < 40, Cu < 50) was obtained from Advent Research Materials Ltd., England. Specimens were prepared by cutting or sawing and a hole was drilled to attach a nylon string. The sample surface was prepared by grinding to 1200 grit with SiC paper and cleaning with ethanol.

The composition of the immersion electrolytes can be found in Table I. Dulbecco's Modified Eagle's Medium (DMEM) is a cell culture medium that is frequently used to assess the corrosion behavior of biodegradable metals in vitro. Besides a 0.1 M NaCl solution, tests were also carried out in inorganic DMEM without $NaHCO_3$. This solution was prepared by adding only the inorganic salts of the DMEM cell culture medium and leaving out the organic constituents. Additionally, DMEM without $NaHCO_3$, that contains

Table I. Electrolyte composition in mg l^{-1} . A detailed concentration overview of the substances contained in the used DMEM electrolyte can be found in the literature.⁵³

Electrolyte	NaCl	KCl	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	CaCl_2	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Amino acids, vitamins, phenol red	Glucose
0.1 M NaCl	5844	0	0	0	0	0	no	0
Inorganic DMEM w/o NaHCO_3	6400	400	200	200	125	0	no	0
DMEM w/o NaHCO_3	6400	400	200	200	125	0.1	yes	1000

all organic constituents like amino acids, vitamins and glucose, was prepared from powder medium (T 041, Biochrom) by adding high-purity water without sterile filtration. DMEM media are usually buffered with the bicarbonate/ CO_2 buffer system. In this work, NaHCO_3 was not added because of possible interference of CO_2 gas evolution with the respirometric method. The initial pH of the three solutions was not adjusted to the physiological value of 7.4 but was ca. 5.8 for 0.1 M NaCl and 5.2 for the DMEM electrolytes.

Gravimetric setups for volumetric corrosion rate monitoring.—

To measure changes in the gas volume gravimetrically with the configuration shown in Fig. 2b, the sample was attached to the hook of a collection container fully made of glass. A thin, monofilament fiber was used to attach the beaker to the balance in order to measure changes in the buoyant force exerted by the changes in gas volume. For more accuracy, it is important to fully submerge the collection setup. Otherwise, possible evaporation of electrolyte would lead to partial emergence of the setup which would cause the measured buoyant force to decrease. A syringe with a bent plastic tube was used to initially remove the air under the collection container. The temperature and atmospheric pressure were logged during the experiments in order to correct for the influences on the gas volume.

The volume-reduced gravimetric setup as in Fig. 2c was constructed from a smaller glass beaker containing the immersed sample with a defined amount of corrosive electrolyte. This beaker was covered by a second, inverted beaker that collects the evolved H_2 gas. While both glass beakers were connected mechanically, a small air headspace separated the immersion electrolyte from the outer electrolyte where the whole assembly was submerged in. A minimum and maximum amount of dissolved H_2 was calculated using the actual H_2 partial pressure in the gas phase and the total pressure of the gas phase, respectively, using Henry's law and a Henry constant of $7.7 \cdot 10^{-6} \text{ mol}/(\text{m}^3\text{Pa})$.⁵⁴

To demonstrate real-time HER monitoring with the different gravimetric setups, Mg alloys AZ31, AM50 and AZ91 were exposed in 0.1 M NaCl for 48 h. The experiments were repeated 2 to 3 times for each alloy and setup. After gravimetric measurements, the corroded sample was removed, and mass gain and mass loss measurements were carried out by cleaning with $200 \text{ g l}^{-1} \text{ CrO}_3$ solution. After the experiment, HNO_3 was added to the immersion solution to dissolve precipitated corrosion products and the solution was filled up with high purity water ($18.2 \text{ M}\Omega\text{cm}$) to make 1000 ml. After further dilution the solution was analyzed with IC (Metrohm 883 Basic IC plus) to determine the concentration of Mg^{2+} ions. The IC device was equipped with a Metrosep C4 – 150/4.0 separation column and the eluent was water with 0.7 mmol l^{-1} dipicolinic acid and $1.7 \text{ mmol l}^{-1} \text{ HNO}_3$. The amount of Mg^{2+} that remained on the sample was estimated from mass gain and mass loss values, assuming $\text{Mg}(\text{OH})_2$ as the dominant corrosion product.

Static setup for manometric corrosion rate monitoring.—

The static setup for simultaneous HER and ORR monitoring is similar to the manometric setup presented in Part I of the paper series. In this setup, the sample was immersed in an electrolyte inside a gas-tight, transparent chamber. A DURAN® laboratory glass bottle was used as a chamber and it was sealed with a DURAN® bromobutyl rubber stopper. In this work, the chamber was submerged in a water bath that was not temperature controlled in order to stabilize the temperature. A Bosch BME 280 combined sensor for absolute pressure, temperature and relative humidity was placed in the air headspace of the vessel. The electronic components of the sensor breakout board were protected from condensation by a coating with a two-component epoxy and additionally wrapped with Teflon tape. The sensor was connected via a gastight feedthrough to an Arduino Uno microcontroller. The O_2 partial pressure was measured both in the liquid phase and in the gas phase with two Piccolo2-OEM optical O_2 meters with contactless sensor spots (PyroScience, Germany) that were glued to the inner wall of the transparent chamber. In some

experiments, a LuminOx LOX-02-S optical O_2 sensor (SST Sensing, UK) was used to measure gas phase O_2 partial pressure and total pressure. This sensor is only applicable for gas phase O_2 monitoring but showed a comparable performance to the PyroScience sensor. Since no RH measurement is possible with the LuminOx sensor, the average RH-time profile of several comparable BME 280 measurements was used in this case. Mixing of the liquid phase was provided by a magnetic stirrer at 200 rpm. The Arduino microcontroller read out both the BME280 sensor and the optical O_2 sensors and the results were returned in a comma separated format. The microcontroller was connected to a computer and the CoolTerm terminal software was used to capture the data to a text file. In addition, a live plotter was developed that enables one to analyze and visualize the data in a real-time graph both on the measurement computer and remotely from anywhere over the internet. The volume of the chamber was determined by weighing the amount of water necessary to completely fill the chamber. The volume of the immersion electrolyte was also determined by weighing. The volume of the gas phase was calculated from the chamber volume minus the volumes of liquid phase, sample, sensor and stir bar. Imaging of the surface during exposure was carried out with a USB microscope PCE-MM 400 in order to construct a time-lapse video of the corrosion progress.

Intermittent-flow ORR monitoring setup.—

A PyroScience optical O_2 sensor was used to monitor the concentration of dissolved O_2 in a chamber completely filled with electrolyte, i.e. without gas headspace. To restore the level of O_2 , the chamber was periodically flushed by pumping fresh aerated solution from an outer electrolyte reservoir. The electrolyte in the reservoir bath was air saturated at the beginning of the experiment. The solution exiting the chamber through an overflow was in contact with air before flowing back to the electrolyte reservoir and was thereby reaerated. The flush pump was triggered automatically by an Arduino microcontroller via a relay module that switches power on or off. A flush phase of 30 s every 30 min was used in most experiments.

The O_2 consumption rate was extracted from the slopes of the sawtooth O_2 concentration curves. As no rate could be determined during the flush phase, it was assumed that the corrosion rate from the previous measurement phase persisted also during this period. The cumulative amount of consumed O_2 was obtained by integrating the rate curves. The cumulative amount of consumed O_2 was compared with the amount of corroded Zn obtained from mass loss in order to calculate the number of exchanged electrons z_{ORR} in the ORR.

To test for background respiration, the O_2 consumption was measured after the experiments when the sample was removed. In DMEM the background O_2 consumption was directly monitored throughout the experiment with a second chamber without sample. Both chambers were flushed by the same pump using a junction and the flush time was increased to 2 min.

Continuous flow-through ORR setup.—

An ORR continuous flow-through setup was constructed using two PyroScience O_2 flow cells with integrated contactless optical O_2 sensor spots that were read out by two Piccolo2-OEM optical O_2 meters. The sensors were located at the inlet and outlet of a respirometric chamber of approximately 25 ml volume that contained the sample. A peristaltic pump supplied a continuous stream of electrolyte. The flow rate was determined gravimetrically and was found to be 32.6 ml per minute.

Mass loss measurements.—

After exposure, to remove the corrosion products, the samples were immersed in a pickling solution (Zn: 250 g l^{-1} glycine solution, Mg alloys: $200 \text{ g l}^{-1} \text{ CrO}_3$) according to ISO 8407.³ The amount of metal loss was determined by weighing the samples before exposure and after removal of the corrosion products with a balance (Mettler Toledo XA205DU). The value was converted to an anodic charge using Faraday's law.

Figure 5. HER charge curves determined from gravimetric H_2 collection measurements of different Mg alloys immersed for 48 h in different volumes of 0.1 M NaCl solution. The measurements of replicate samples are normalized to the sample area, averaged and plotted together with the standard deviation. Although the 50 ml samples actually corroded less compared to the 500 ml samples, more H_2 was detected because of a reduced influence of H_2 dissolution (see Fig. 7).

Results and Discussion

Gravimetric volumetric experiments.—The influence of temperature and ambient pressure on the baseline of gravimetric experiments was already reported before. After correcting for environmental fluctuations, the gravimetric method exhibits a good reproducibility and is sensitive enough to monitor HER rates in the low μA range. Gravimetric measurements of three different Mg alloys were carried out with the regular gravimetric setup (Fig. 2b) to monitor HER rates in real-time with the samples being immersed in 500 ml of 0.1 M NaCl. Additional measurements with the volume reduced gravimetric setup depicted in Fig. 2c were carried out to test the influence of the immersion electrolyte volume to surface area on the corrosion rate and on the amount of dissolved H_2 .

From the gravimetric results shown in Fig. 5 it can be seen that the corrosion rate decreases with an increase in the amount of Al in the alloy, with AZ91 samples evolving the lowest amount of H_2 . A similar trend of decreasing global corrosion rate with increasing Al content was also observed by Bland et al.⁵⁵ While the microstructure of AZ31 is characterized by α -Mg with Al-Mn intermetallic particles, AM50 and AZ91 contain a β -Mg₁₇Al₁₂ second phase as well as eutectic $\alpha + \beta$. These intermetallic phases in Mg alloys act as cathodes. Therefore, they may initiate microgalvanic corrosion in the surrounding alpha matrix and lead to higher extent of localized attack.⁵⁵ On the other hand, the β -phase can act as a barrier for the lateral propagation of filiform corrosion fronts.⁵⁶ While the β -phase is absent in AZ31, its volume fraction increases from AM50 to AZ91. Another influence that determines the corrosion rate of Mg–Al alloys is the Al content in α -Mg.⁵⁷ Consequently, the trend of increasing corrosion resistance might be explained by a higher Al content in the α -phase and the increasing barrier effect of the β -phase.

From the slope of the charge curves the real-time HER rate was calculated as shown in Fig. 6. For AZ31, a strong increase in corrosion rate at the beginning of the 500 ml experiments was observed. Parallel optical imaging of the surface revealed that the increase in HER rate coincides with an increase in the number of active corrosion fronts that propagate across the sample. This behavior is diminished for the lower electrolyte volumes. As with AM50 and AZ91, the corrosion rate of AZ31 in the 50 ml and 13 ml setup shows a decline with immersion time. This is probably due to a faster increase of the solution pH that facilitates the precipitation of Mg(OH)₂ on the sample surface and leads to an increased

Figure 6. Comparison of real-time HER current density of (a) AZ31, (b) AM50 and (c) AZ91 samples in 0.1 M NaCl obtained with gravimetric setups of different surface area to electrolyte volume ratios. Average curves of multiple replicate samples are shown together with the standard deviation. Note that the curves show only H_2 detected by the balance and are not corrected for dissolved H_2 . A comparison with mass loss and the estimation of the contribution of H_2 dissolved in the liquid phase is given in Fig. 7.

Figure 7. Comparison of the total consumed charge after 48 h of immersion in 0.1 M NaCl as determined by gravimetric HER monitoring, solution analysis for dissolved Mg^{2+} ions with ion chromatography, and mass loss. The amount of Mg^{2+} in the corrosion film was estimated from mass gain and mass loss.

Figure 8. Gravimetric experiment of Zn corrosion in 0.1 M NaCl with simultaneous O₂ sensor measurement using the setup in Fig. 2d.

protectiveness against corrosion. Thus, the surface area to electrolyte volume modifies the corrosion mechanism that occurs as well as the total amount of corrosion.

Apart from the activation of corrosion fronts at the beginning of AZ31 corrosion, the HER rates recorded with the 50 ml setup seem to be higher compared to the 500 ml experiments, also for AM50 and AZ91. That this interpretation is slightly misleading can be explained by comparing the total amount of consumed HER charge after 48 h immersion in 0.1 M NaCl with the mass loss method (Fig. 7). Comparing the amount of H₂ collected with the 500 ml setup with mass loss reveals a substantial discrepancy. For this setup, HER monitoring with AZ31 detected only 44% of the mass loss charge and less than 25% in the case of AM50 and AZ91. The discrepancy was attributed to the loss of gaseous H₂ by dissolution into the solution. When H₂ is dissolved it does not exert a buoyant force anymore and is thus not detected by the gravimetric method. An alternative explanation that could contribute to the discrepancy with mass loss could be that ORR plays a partial role in the corrosion mechanism. Looking at the results with 50 ml and 13 ml electrolyte volume show that the correlation of the amount of detected H₂ to the amount of mass loss gets much closer compared to the 500 ml setup. Samples exposed in the volume reduced gravimetric setups show a lower overall amount of corrosion as determined by mass loss for all three Mg alloys. However, more H₂ gas evolution is detected for the 50 ml experiments. This implies that, with the 500 ml setup a big amount of H₂ gas is not detected because of dissolution of H₂ into the electrolyte.

To further assess the issue of H₂ dissolution, two types of dissolved H₂ estimations were performed with Henry's law as shown in Fig. 7. The values denoted with H_{2liq}^{max} are HER equivalent charge values that represent the amount of H₂ dissolved in the liquid phase that was calculated assuming that the solution is in equilibrium with a gas phase of pure H₂ with a pressure equal to the atmospheric pressure. This could be the case for H₂ collected in the 500 ml setup where there is no gas headspace. For the volume reduced experiments with a gas headspace, the H_{2liq}^{min} values were calculated assuming that the concentration of dissolved H₂ is in equilibrium with the actual partial pressure of H₂ in the headspace. Since the gas evolved from the samples is pure H₂ at atmospheric pressure before it reaches the headspace, the H_{2liq}^{max} value could be a plausible scenario also for the headspace setup. The true H₂ solubility could be ascertained with a sensor for dissolved H₂ in future work. The results show that the amount of H₂ that could potentially dissolve in 500 ml

Figure 9. Simultaneous HER and ORR monitoring of AZ91 immersed in 0.1 M NaCl in the manometric respirometric setup: (a) raw data obtained from the sensors, (b) changes in the number of H₂ and O₂ in gas and liquid phase, and (c) HER, ORR and total respirometric charge and current density.

of electrolyte by far exceeds the amount of H₂ gas detected in the experiments. This makes it difficult to estimate the contribution of dissolved H₂ for this setup without additional mass loss tests.

Conversely, the influence of possible H₂ dissolution is limited in the volume reduced experiments. As a consequence, more H₂ is detected and it is possible to give a good estimate of the amount of dissolved H₂ with Henry's law. This shows that the effect of dissolution of H₂ should be considered especially for low corrosion rates and high volume of electrolyte. More sensitive and correct measurements of HER rates are possible with a volume reduced gravimetric setup as shown in Figs. 2c, 2d. This comes at the expense of a possible modification of the corrosion mechanism due a faster alkalization with higher surface area to volume ratio setups.

Regarding the amount of corrosion as determined by solution analysis with ion chromatography it can be observed that this method largely underestimates the amount of corrosion that has occurred. This can be rationalized with the Mg²⁺ ions that form a corrosion product film on the sample surface and that are not registered by solution analysis. The amount of corrosion products that remained on the sample were estimated with mass gain and

Figure 10. HER (a) and ORR (b) charge curves of Mg alloys in 0.1 M NaCl, inorganic DMEM w/o NaHCO₃ and DMEM w/o NaHCO₃ measured with the manometric respirometric setup. Dissolved H₂ was considered in the HER charge with a correction based on Henry's law using the actual partial pressure of H₂ in the gas phase.

mass loss measurements and assuming that Mg(OH)₂ was formed as the dominant corrosion product. From Fig. 7 it can be seen that this estimation gives a good fit of the amount of soluble and insoluble Mg²⁺ ions with mass loss, especially for AZ31. The remaining discrepancy with AM50 and AZ91 can be explained with the increasing amount of corroded Al³⁺ ions that were not measured with IC and that were not considered with the corrosion product composition assumption. Compared with the 500 ml samples, the lower electrolyte volume samples exhibited proportionately more Mg²⁺ ions in the film, which supports the notion of increased protectiveness of the corrosion product film under these conditions.

With only gravimetric HER measurements, one uncertainty remains regarding the role of the ORR in Mg alloy corrosion under immersion conditions. In Part I of this paper series, for atmospheric corrosion, it was found that ORR can contribute to the cathodic reactions on Mg alloy corrosion. Already with the gravimetric results in conjunction with mass loss it can be stated that ORR has a minor influence during 48 h immersion. The addition of an optical O₂ sensor that measures O₂ partial pressure in the headspace of the gravimetric setup would be a possibility to measure both HER and ORR simultaneously. This measurement configuration was tested on Zn immersed in 0.1 M NaCl using the setup in Fig. 2d and the results are shown in Fig. 8. Under neutral conditions, ORR is the dominant cathodic reaction of Zn corrosion. The ORR leads to the removal of O₂ from the headspace that can be detected with both the gravimetric measurement and the O₂ sensor. The concentration changes of O₂ in the liquid phase were not monitored in this experiment. Because the electrolyte was stagnant, the corrosion rate was extremely low in this experiment. While there is some deviation in the signals of the two

measurement approaches in the beginning of the experiment, a very good agreement in the ORR rate was found after one day.

One possible source of error is that the optical fiber was not tightly attached to the sensor spot in order not to disturb the gravimetric measurement. The exact position of the optical fiber on the sensor spot could influence the measured O₂ pressure. In addition, the O₂ sensor measurement is not independent from the gravimetric measurement since any volume change also affects the O₂ partial pressure. To study the influence of ORR in Mg alloy immersion in more detail, it was decided to carry out tests in the constant gas volume manometric setup.

Static manometric experiments.—To demonstrate simultaneous HER and ORR monitoring with the static manometric setup, the results of a 90 h immersion experiment carried out with AZ91 in 0.1 M NaCl is shown. The raw data recorded with the different sensors can be seen in Fig. 9a. From the changes in O₂ partial pressure in the gas and liquid phase, total pressure, temperature and relative humidity it is possible to calculate the change in the number of H₂ and O₂ molecules in the gas phase and liquid phase (Fig. 9b). To calculate the number of H₂ in the gas phase, the total pressure change is corrected for changes in water vapor pressure and changes in O₂ partial pressure. The amount of H₂ dissolved in the liquid phase is estimated with Henry's law using the actual partial pressure of H₂ in the gas phase. In this special long-term experiment, besides evolving H₂, AZ91 also consumes a considerable amount of O₂. This can be seen from the decrease in O₂ partial pressures and in the decrease in the total number of O₂ molecules. In Fig. 9c, the change in the total number of moles of H₂ and O₂ is converted to an HER and ORR charge assuming $z_{\text{ORR}} = 4$. The derivative of the charge curves results in real-time current density for the two cathodic reactions. This demonstrates that real-time monitoring of both HER and ORR rates is possible simultaneously.

Looking at the comparison of the total respirometric charge with mass loss reveals an excellent correlation. The share of ORR in the cathodic charge for this particular long-term experiment was over 40%. A special phenomenon that was revealed by real-time monitoring in this experiment is that the corrosion rate and especially the ORR rate increased again after an initial period of declining corrosion rate. Parallel optical imaging of the corroding surface (see time-lapse video in supporting information) demonstrates that this event coincides with a branching and multiplication of active corrosion fronts. It can only be speculated that this activation of corrosion fronts was triggered by an increased cathodic activity that supplied the current necessary to drive more anodic fronts.³⁸ Since the effect of a second corrosion rate maximum was not reproducible on AZ91, it is possible that a special feature in the microstructure that results from the inhomogeneous casting process was responsible. Subsequently, many of the corrosion fronts came to a stop which leads to decreasing of the HER and ORR rates. Interestingly, afterwards the deposition of a white precipitate can be observed on parts of the sample and no ORR activity was detected anymore. It is possible that the precipitates blocked sites where the ORR was occurring.

In general, the partial pressure of O₂ in the liquid phase tends to follow the course of partial pressure in the gas phase, which means that gas exchange is fast enough and the concentration in both phases is in equilibrium. Removal of O₂ from the liquid phase can be observed in the parts of the experiments with high H₂ evolution rate. H₂ gas takes up dissolved O₂ and leads to a degassing of the surrounding solution. Eventually though, the bubbles will rise to the gas phase and the solution will again reach equilibrium with the concentration in the gas phase. In the gas-tight chamber, O₂ cannot escape the closed system, unless it is really consumed by corrosion. Comparing the changes in the moles of O₂ in gas and liquid phase, it becomes obvious that most changes occur in the gas phase. In a stirred solution and for the ratio of gas to liquid volume used in this experiment, it seems that one O₂ sensor that measures in the gas

Figure 11. Comparison of the results of the manometric respirometric experiments with mass loss after 48 h immersion. The relative contribution of $Q_{\text{HER}}/Q_{\text{tot}}$ and $Q_{\text{ORR}}/Q_{\text{tot}}$ are given in percent in addition to the values of $Q_{\text{tot}}/Q_{\text{ML}}$ in percent.

Figure 12. Simultaneous HER and ORR monitoring of a hot-dip galvanized steel sample with scratches and cut edges immersed in 1 M NaCl solution. A time-lapse video can be found in the supporting information.

phase would be sufficient to monitor O₂ consumption. Since the changes in the moles of O₂ in the liquid phase are not very pronounced, this contribution could be calculated with adequate accuracy from the O₂ partial pressure in the gas phase.

More manometric experiments of AZ31 and AZ91 Mg alloys were carried out in 0.1 M NaCl, in a solution that contained the inorganic parts of DMEM without NaHCO₃ and in DMEM without NaHCO₃ for an exposure time of 48 h. The resulting averaged HER and ORR charge curves of multiple replicate samples are depicted in Fig. 10. NaHCO₃ was not added to the DMEM electrolyte because of possible interference with the pressure measurements by out-gassing CO₂. DMEM is a cell culture medium that contains organic molecules such as amino acids, vitamins and glucose as nutrients for cell growth. Unfortunately, this medium favors also the growth of microorganisms and their metabolism can lead to considerable background respiration. The influence of background respiration was determined by parallel experiments without a sample and by testing the solution at the end of the experiment with the sample removed. It was found that the high pH that evolved due to Mg corrosion effectively suppressed the growth of microorganisms for the duration of the experiment, which is in accordance with literature.⁴¹

Figure 13. Intermittent-flow respirometric determination of O₂ consumption of Zn immersed in 0.1 M NaCl. The O₂ concentration curve shows a sawtooth shape that is the result of alternating 30 min measurement periods and 30 s flush periods. The O₂ consumption rate was extracted from the slopes of the measurement periods.

AZ91 is less susceptible to corrosion in 0.1 M NaCl compared to AZ31. This trend that was already found with the gravimetric measurements can be confirmed with the manometric method. In addition, with the manometric setup it is possible to quantify the amount of O₂ that was consumed due to the ORR in real-time. For 48 h immersion, the influence of ORR is not as pronounced as in the 90 h experiment in Fig. 9. However, a small but steady O₂ consumption can be resolved with the O₂ sensors for all alloys and solutions.

Comparing the influence of the different electrolytes for AZ31, it follows that the HER and ORR rates increase in the order: inorganic DMEM without NaHCO₃ < 0.1 M NaCl < DMEM without NaHCO₃. This can be explained, on the one hand, with the formation of corrosion product layers with the ions present in the DMEM medium. For example, it is commonly observed that Mg in simulated physiological solutions forms an amorphous layer of (Mg,Ca)_x(PO₄)_y(CO₃)_z(OH)_i that can increase the protectiveness afforded to the substrate.^{59–61} On the other hand, it seems that amino acids and the other organic compounds present in the DMEM electrolyte have an accelerating effect on the corrosion rate of AZ31. This could be explained by the chelating interaction of the organic molecules with Mg²⁺– or Ca²⁺– ions that can encourage Mg dissolution and retard the formation of insoluble surface layers.⁶²

A comparison of the HER, ORR and total respirometric charge with mass loss charge for the different samples is carried out in Fig. 11. A very good agreement between the total respirometric charge and mass loss was found. This implies that reliable real-time monitoring is possible with the manometric respirometric method and that the cumulative amount of HER and ORR charge gives a good measure for the amount of corrosion that has occurred. In general, the contribution of ORR to the total cathodic charge is around 10%. These findings are in line with recent studies that provide evidence for the partial role of ORR in Mg corrosion under

Figure 14. Intermittent-flow experiment of Zn immersed in DMEM w/o NaHCO_3 where the rate of microbial background respiration was determined simultaneously in a parallel chamber without sample. Subtracting the background O_2 consumption from the consumption measured in the sample chamber leads to the true O_2 consumption of the corroding sample.

Figure 15. Comparison of the ORR charge determined from O_2 consumption with mass loss charge for several intermittent-flow experiments in different electrolytes. The immersion time was 72 h for 0.1 M NaCl and inorganic DMEM w/o NaHCO_3 and 20 h for the DMEM w/o NaHCO_3 experiment. The ORR charge ranges for z_{ORR} values of 2 and 4 are given together with the apparent z_{ORR} that was calculated from mass loss and cumulative consumed O_2 .

immersion conditions.^{63,64} Under the exposure conditions of the present study, no considerable difference of the ORR influence was found for the different Mg alloys or the different electrolytes. Some scattering between replicate samples was found in the ORR percentage, which can possibly be explained by a variation in the microstructure or in the level of impurities of the samples. To conclude, the influence of ORR in Mg alloy immersion corrosion cannot be omitted in general. The AZ91 90 h experiment in Fig. 9 signifies that there are conditions where the ORR contribution can be substantial.

Another example measurement with the manometric setup was carried out with a hot dipped galvanized steel sample with scratches and cut edges immersed in 1 M NaCl solution (Fig. 12). A time-lapse video can be found in the supplemental material. The onset of visible H_2 evolution can be observed after an initial phase of corrosion accompanied by only ORR. Neither Zn nor steel show appreciable amount of HER at open circuit corrosion at this pH value, so the effect was attributed to cathodic polarization of Fe by

the galvanic coupling to Zn.⁶⁵ The onset of HER could be also followed with the respirometric measurement in real-time. With further immersion time, it was found that the HER rate increased and eventually surpassed the progressively decreasing ORR rate.

Intermittent-flow respirometric experiments.—Intermittent-flow experiments to monitor O_2 consumption rates are very well suited to study corrosion systems where ORR is the only cathodic reaction. This method works without a gas phase and monitors the decrease of the dissolved O_2 concentration with an optical O_2 sensor. Because the solubility of O_2 in water is limited, the partial pressure and hence the concentration of dissolved O_2 decreases faster than in experiments with a gas phase. This allows for sensitive measurements of O_2 consumption but also requires a periodic replenishing of the O_2 content in the chamber for long-term monitoring. An example measurement of Zn corroding in 0.1 M NaCl is demonstrated in Fig. 13. A series of 30 min. O_2 consumption measurement periods was periodically interrupted by 30 s flushing intervals to replace the electrolyte inside the chamber. The solution inside the chamber was stirred with 200 rpm to avoid bulk O_2 concentration gradients. O_2 consumption rates were extracted from the slopes of the concentration profiles of each measurement period. Careful inspection of the data and the quality of the fit is crucial in getting reliable results. Temperature imbalance and gas bubbles can skew the results and should be avoided. Integration of the obtained rates leads to a cumulative amount of O_2 consumed by the corroding sample.

While background O_2 consumption was minimal in the case of 0.1 M NaCl, it became substantial in an experiment of Zn immersed in DMEM w/o NaHCO_3 (Fig. 14). In this intermittent-flow experiment the rate of microbial background respiration was determined simultaneously in a parallel chamber without a sample. After 12 h immersion an exponential increase of the O_2 consumption rate in the background chamber was recorded. This increase in background respiration affects also the rates measured in the sample chamber. Subtracting the background O_2 consumption from the consumption in the sample chamber leads to the true O_2 consumption of the corroding sample, assuming there was no effect of Zn corrosion on the background. The experiment was stopped when the background rate became comparable to the consumption rate of the sample.

In addition to 0.1 M NaCl and DMEM w/o NaHCO_3 , intermittent-flow experiments were also conducted with inorganic DMEM w/o NaHCO_3 . The total amount of consumed O_2 of these experiments was compared with the charge determined independently by mass loss in Fig. 15. It was found that the ORR charge calculated with $z_{\text{ORR}} = 4$ would largely overestimate the amount of corrosion that has occurred as determined by mass loss. The results suggest that the ORR proceeds to a high extent via the 2-electron mechanism. In fact, many studies agree that the 2-electron ORR mechanism predominates on Zn covered by oxide or hydroxide surface layers under near neutral conditions.^{66–70} The 2-electron ORR mechanism leads to the generation of H_2O_2 that goes into the bulk solution. From a measurement point of view, it is then important whether the produced H_2O_2 is stable in the solution or decomposes before or after being flushed out of the measurement chamber. If two H_2O_2 molecules decompose to O_2 and water inside the chamber, this will contribute to the 4-electron pathway. If the same reaction happens outside the chamber, it will appear like a 2-electron pathway mechanism because the generated O_2 molecule is out of the reach of the O_2 sensor.

The fate of the peroxide intermediate may depend on the catalytic properties of the material where the ORR takes place. Various metals were screened for their selectivity of the 2-electron pathway or the 4-electron pathway with a polarographic method by Delahay.⁶⁷ Furthermore, rotating ring disc electrode (RRDE)^{68,69} experiments or scanning electrochemical microscopy (SECM)^{37,71} approaches enable one to probe for the amount of H_2O_2 to elucidate the ORR mechanism. Even for one material the potential or pH dependent surface state can change the ORR mechanism.^{66,68,69} On

Figure 16. Real-time ORR current densities calculated from the slopes of the O_2 consumption curves in intermittent-flow experiments of Zn immersed in different electrolytes. The apparent z_{ORR} was used for the calculation of ORR rates.

Figure 17. Continuous flow-through respirometric monitoring of O_2 consumption of a Zn sample corroding in 0.1 M NaCl.

Pt, the mass transport rate and the presence of adsorbing species in the electrolyte can influence whether H_2O_2 gets further reduced on the electrode or desorbs and can diffuse away.⁷² Other influences that affect the stability of H_2O_2 , once it reaches the bulk, are peroxide concentration, pH and temperature of the solution, as well as the presence of homogeneous or heterogeneous catalysts that favor H_2O_2 decomposition.^{71,73,74} This can be for example the presence of Fe^{3+} ions,⁷⁵ Cu^{2+} ions,⁷³ or I^- ions.⁷⁴

A color test based on a specific detection reaction for the presence of H_2O_2 was carried out by adding $TiOSO_4$ dissolved in dilute sulfuric acid to a 0.1 M NaCl solution where Zn was corroding for 24 h.⁷⁶ This test showed a clear yellow color that is the result of the formation of a peroxotitanium complex.⁷⁷ The positive test confirms the presence of H_2O_2 in the bulk solution that was produced by Zn corrosion. It is therefore concluded that, under the experimental conditions of the intermittent-flow experiment, H_2O_2 was produced as a stable product. H_2O_2 entered the bulk solution in the chamber without extensive further reduction to water or decomposition. Periodic flushing led to a dilution with the electrolyte from the reservoir and prevented H_2O_2 accumulation to a level

where decomposition was fast enough to enable a 4-electron ORR pathway.

An apparent number of transferred electrons z_{ORR} was calculated, assuming that both mass loss and respirometry give reliable values of the number of oxidized Zn ions and number of reduced O_2 molecules, respectively. The calculated values, given in Fig. 15, are close to 2 for 0.1 M NaCl and inorganic DMEM. The Zn experiment with DMEM electrolyte showed a higher z_{ORR} value of 3.2. A possible explanation for the higher value is that the presence of organic molecules favored the catalytic decomposition of peroxide. In addition, in contrast to the other electrolytes, DMEM contains a small amount of Fe^{3+} -ions that could have catalyzed the decomposition of H_2O_2 . If the ORR mechanism changes during exposure time, also the shorter duration of the DMEM experiment could explain the higher z_{ORR} value. To compare the real-time corrosion rates of Zn in the different solutions, it was decided to evaluate the ORR rates with z_{ORR} values that were calculated individually for each sample based on mass loss and cumulative O_2 consumption. From the current density curves in Fig. 16 it follows that 0.1 M NaCl has the lowest Zn corrosion rate. The ORR rates are higher in inorganic DMEM and greatly accelerated in DMEM with organic constituents. The origin of this behavior, i.e. the role of the different components in the complex electrolytes on the corrosion mechanism remains to be elucidated.

It is interesting to note that a contribution of the 2-electron process was not found under atmospheric corrosion conditions in Part I of the paper series. For Zn corroding under deliquesced NaCl droplets, the data suggests that ORR proceeds solely through the 4-electron process. The situation with a thin electrolyte layer probably favors the decomposition or further reduction of peroxide. Future work should focus on the effect of different experimental parameters on the contribution of the peroxide pathway for different materials.

Continuous flow-through respirometric measurement.—Pure Zn in a respirometric chamber was exposed to a continuous stream of 0.1 M NaCl solution in a flow-through experiment (Fig. 17). Real-time O_2 consumption rates due to corrosion were determined from the concentration difference of the incurrent and excurrent stream and the flow-rate. Integrating the rates results in the cumulative amount of consumed O_2 . Similar to the intermittent-flow experiments, it is possible to calculate the number of exchanged electrons in the ORR using the mass loss results. For this experiment, a z_{ORR} value of 3.7 was found which is much closer to the 4-electron pathway compared to the intermittent-flow experiments in the same electrolyte. ORR rates plotted in Fig. 17 were calculated with this apparent z_{ORR} value. Differences in the experimental conditions that could possibly explain the different z_{ORR} value found in the continuous flow setup compared to intermittent-flow experiments include the following points. Due to a higher surface area to chamber volume ratio it can be expected that a higher peroxide concentration builds up in the chamber. The reduced flow velocity in the flow-through experiment favors a more laminar type of electrolyte flow over the corroding surface. Because of the limited mixing of the solution in the vicinity of the sample surface with the bulk solution, this situation resembles the atmospheric corrosion scenario. As a consequence, it can be hypothesized that the slower mass transfer conditions increases the possibility of further H_2O_2 reduction or decomposition. This example however demonstrates that mechanisms of corrosion reactions can be highly sensitive to details in the experimental setup. This clearly illustrates the necessity to collect detailed data under different exposure conditions, such as is possible by the here introduced methodologies.

Conclusions

Our work demonstrates with different respirometric methods that immersion corrosion kinetics can be monitored non-destructively and in real-time. The respirometric method is recommended as a

valuable addition to the well-established electrochemical techniques to study corrosion processes. As conclusions we find:

- Gravimetric real-time measurement of the evolved H_2 volume enables sensitive monitoring of HER rates. H_2 dissolved into the electrolyte can pose difficulties in accurate measurement of corrosion resistant alloys in high volume of electrolyte. Volume reduced and closed setups were presented that allow for a correction of the amount of dissolved H_2 with Henry's law. With a headspace setup, gravimetric ORR monitoring is possible.

- A combined pressure sensor and optical O_2 sensor manometric setup was presented that allows for real-time monitoring of HER, ORR or both reactions simultaneously. The method was applied to study the effect of different physiological solutions on Mg alloy corrosion and to monitor ORR and HER rates of a scratched Zn coated steel.

- The gravimetric and manometric respirometric methods were validated by an excellent correlation between the total cathodic charge and mass loss.

- It was shown that O_2 is consumed during Mg alloy corrosion also under immersion conditions. Under the experimental conditions studied, the share of ORR was around 10% of the total cathodic charge. In a longer-term immersion experiment with AZ91, over 40% ORR corrosion was detected. The influence of ORR should be taken into account in future studies.

- The concepts of intermittent-flow and flow-through respirometry were successfully adapted in order to monitor O_2 consumption rates in corrosion systems where ORR is the dominant reaction. Example measurements with Zn in different physiological solutions were presented.

- For Zn, the ORR mechanism can lead to the generation of H_2O_2 as a stable product according to a 2-electron ORR pathway. Thus, the conversion of O_2 consumption rates to ORR corrosion rates is not straightforward. More work is needed to identify the contributions of the ORR pathways for different metals under various experimental conditions.

Acknowledgments

M.P.B. gratefully acknowledges financial support by the German Research Foundation (DFG) via the research training group GRK 1896. The authors thank Martin Kolacyak for technical support.

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